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(72) Inventor VINCENT LAMBERTI



(54) SULFOSUCCINATE DERIVATIVES FOR USE AS DETERGENT BUILDERS

We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London, E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

Eutrophication is the process of excessive fertilization of aquatic plants through enrichment of waters with nutrients, such as carbon, nitrogen, phosphorus, potassium, iron, trace

metals and vitamins.

Although there is no present adequate proof, it has been postulated that the phosphoruscontaining builders present in detergent compositions can be a factor in eutrophication. Therefore any substitutes which do not contain phosphorus may decrease to some extent the eutrophication.

It is therefore an object of the present invention to provide novel compounds which are useful as detergent builders. It is another object of the present invention to provide novel compounds which function as surface active agents and as detergent builders.

It has now been discovered that the alkali metal, ammonium and substituted ammonium salts of certain sulfoaliphatic dicarboxylic 30 acids can serve as effective detergent builders in detergent compositions. Many of these detergent builders and their acid forms are novel and they are generally described as α - substituted - β - sulfosuccinic acids, and alkali metal, ammonium and substituted ammonium salts thereof, having the general formula:

wherein Z is O, S, SO, SO₂

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or NR_1 ; R is (C_1-C_{10}) alkyl, (C_1-C_{10}) hydroxyalkyl or (C_2-C_{10}) alkoxyalkyl; phenyl; carboxy-substituted or mono-, di- or tri-alkyl-substituted phenyl, wherein each of the alkyl group or groups contains 1-4 carbon atoms; sulfoalkyl or carboxyalkyl, wherein the alkyl moieties contain 1-4 carbon atoms; or R'Z(CH₂CH₂O)_n—CH₂CH₂—, wherein R' is hydrogen or alkyl containing 1-24 carbon atoms; and n is 0 or an integer of from 1-15; and when Z is

or NR1, the groups R may be joined with the nitrogen atom to form a morpholinyl group, and when Z is O and the group R is an alkyl group the latter contains 2-30 carbon atoms.

Thus, specific compounds and classes of compounds embraced by the generic formula

above include:

(I)

 α - alkoxy - β - sulfosuccinic acids 60 α - phenoxy - β - sulfosuccinic acids α - carboxyphenoxy - β - sulfosuccinic acids α - alkylphenoxy - β - sulfosuccinic acids α - carboxyalkoxy - β - sulfosuccinic acids α - sulfoalkoxy - β - sulfosuccinic acids 65 α - alkoxyethoxy - β - sulfosuccinic acids α - alkoxypolyethyleneoxyethoxy - β - sulfo-

succinic acids α - hydroxyalkoxy - β - sulfosuccinic acids;

the alkali metal, ammonium and substituted ammonium salts thereof; and the thio, sul-

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finyl and sulfonyl analogs of all the foregoing compounds wherein the oxygen group
attached to the α-carbon of the succinic acid
or succinate moiety is replaced by —S—,
—SO— or —SO₂—, respectively, and/or
wherein the cases of the α-alkoxyethoxy compounds and the α-alkoxypolyethyleneoxyethoxy
compounds the oxygen attached to the alkyl
group (R') is replaced by —S—, —SO— or
—SO₂—.

In accordance with a specific aspect of the present invention are the nitrogen containing α - substituted - β - sulfosuccinic acids, and the alkali metal, ammonium and substituted ammonium salts thereof, having the following general formula:

$$R - N - CH - CH - SO_{i}H$$
 R_{i} COOH COOH

wherein the groups R and R₁ may be the same or different and R₁ is C₁ to C₂₀ alkyl, C₁ to C₄ hydroxyalkyl, carboxymethyl, carboxyethyl, sulfomethyl or sulfoethyl, or R and R₁ may be joined with the Nitrogen atom to form a morpholinyl moiety; and R₁ is hydrogen or R.

Representative compounds and classes of compounds embraced by generic Formula II above include:

 α - alkylamino - β - sulfosuccinic acids such as α - methylamino, α - propylamino, α - octylamino and α - laurylamino - β - sulfosuccinic acid;

 α - dialkylamino - β - sulfosuccinic acids such as α - dimethylamino, α - ethylmethylamino, α - methylhexylamino and α - dioctylamino - β - sulfosuccinic acid;

 α - hydroxyalkylamino - β - sulfosuccinic acids such as α - hydroxyethylamino, α - hydroxybutylamino and α - bis(hydroxyethyl)amino - β sulfosuccinic acid;

 α - carboxyalkylamino - β - sulfosuccinic acids such as α - carboxymethylamino, α - carboxyethylamino - β - sulfosuccinic acid and the corresponding sulfo analogs;

 α - morpholinyl - β - sulfosuccinic acid; and the mono or poly salts thereof.

In accordance with further specific aspect of the present invention are the amine oxide derivatives of Formula II, wherein the nitrogen is a tertiary atom, corresponding to the general formula:

wherein the groups R may be the same or different and are as designated in Formula II. As will be appreciated by those skilled in the art, the compounds of the invention contain at least two asymmetric carbon atoms and therefore can exist in several optically active forms as well as optically inactive mixtures (racemates). For purposes of this invention, the compounds as defined are intended to include all of the stereoisomeric forms and mixtures thereof.

In addition to the detergent building properties exhibited by the entire class of compounds described above, certain select members also exhibit properties which make them useful as wetting and foaming agents and thus constitute a class of novel surface active agents. For example, the α-alkoxy-β-sulfosuccinic acids and the thio analogs, containing from about 1—8 carbons, preferably from 1 to about 4 carbon atoms, exhibit excellent detergent building properties whereas the higher homologs containing from about 9—30 and more preferably 9—24 carbon atoms in the alkyl chain, additionally exhibit wetting, foaming and detergency properties.

Similarly, the α - alkoxyethyl and α -alkoxypolyethyleneoxyethoxy - β sulfosuccinic acid compounds containing from about 9—30 and preferably about 9—24 carbon atoms in the alkoxy moiety are also useful as wetting agents, foaming agents and detergents as well as detergent builders.

Although the builders of the present invention may be utilized as the free acid provided sufficient alkaline additives are included in the detergent composition to convert the acid forms in situ to the normal salt forms, the alkali metal, ammonium and substituted ammonium salts of the α-substituted-β-sulfosuccinic acids are preferred. Included in the substituted ammonium salts that can be employed are the monoethanolammonium, diethanolammonium, triethanolammonium, methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, morpholinium, N-methylmonoethanolammonium and N-ethylmonoethanolammonium salts and mixtures thereof.

The utility of the compounds of the present invention is not only reflected in terms of excellent building and biodegradability properties but also in low cost of preparation, since they are prepared from readily available and inexpensive materials. For example, the compounds of this invention are derived from sulfomaleic anhydride and readily available alcohols, thiols, hydroxy acids and amines.

More specifically, the compounds of this invention are reaction products derived by reaction between sulfomaleic acid and compounds having an active hydrogen atom.

Compounds having an active hydrogen atom and suitable for use in preparing the compounds of the present invention are monodi- or polyhydric alcohols and mono- di- or polyhydroxy acids and their sulfur-containing

analogs. Suitable examples of the aforeform the α - substituted amino - βmentioned monohydric alcohols include alkoxysulfosuccinates include: alkanols such as methoxyethanol and the linear primary and secondary alcohols conethanolamine taining up to 30 carbon atoms and their thio diethanolamine analogs; aromatic hydroxy compounds parpropanolamine ticularly the carbocyclic mono- and bicyclic morpholine 70 aromatic hydroxy compounds, such as naph-N-methylethanolamine thols and phenols and the mono- di- or triglycine C₁—C₄ alkyl ring substituted derivatives thereof. Suitable examples of dihydric alcohols alanine N-methyl taurine include the glycols such as ethylene glycol, alkylamines containing 1-20 carbons in the propylene glycol, butylene glycol, trimethylene alkyl chain, as well as other amines having glycol, tetramethylene glycol, pentamethylene a replaceable or active hydrogen and a glycol, hexamethylene glycol, heptamethylene basicity comparable to the aforementioned glycol, long chain 1,2-diols containing from 8-30 carbon atoms and aromatic carbocyclic glycols such as phenylethylene glycol. Simil-In particular the α -amino substituted- β -sulfosuccinates derived from water-soluble arly, suitable polyhydric alcohols include 20 glycerol, pentaerythritol, hexanetriol, sugars amines may be prepared by reacting in aqueous and their thio analogs. solution without the aid of heat and those In addition to the alcohols, the hydroxy derived from water insoluble amines (i.e., carboxylic and sulfonic acids (in their ester higher alkylamines) are reacted in a mixed and acid/salt forms, respectively) may also solvent system such as ethanol/water or direact with sulfomaleic anhydride and sulfooxane/water at temperatures ranging from maleic acid. These include glycollic, lactic, about 25° C to about 80° C; isolation from glyceric, hydroxypropionic, salicyclic and merthe reaction medium, and purification if desired, being effected by conventional capto acetic acid, hydroxymethanesulfonic acid and hydroxyethanesulfonic acid. methods. 30 Still another important class of compounds The compounds wherein the α -substituent is containing active hydrogen are ethylene oxide joined to the a-carbon atom by an amine adducts of C₁ to C₂₀ primary and secondary alcohols with 1—15 moles of ethylene oxide. oxide group (as in Formula III) may be prepared by reacting the tertiary amine com-In general, the α - substituted - β - sulpounds of Formula II with oxidizing agents fosuccinate salts, wherein the a-substituent is such as hydrogen peroxide, peroxyacetic and joined to the a-carbon atom of the sulfoperoxyformic acid in the manner described succinate moiety by an O or S linkage, may for oxidizing tertiary amines by Hoh et al., be prepared by heating at a temperature of from about 25 to 120° C, preferably 60 to J. Am. Oil Chemists' Soc., 40, 268 (1963). 100 In preparing the sulfosuccinate salts from 100° C, sulfomaleic anhydride with a suitable the free acid, the amount of base utilized will compound having an active hydrogen atom as determine whether the mono- di- or tri-salt described above followed by further treatment is obtained. For example, the use of one mole with a base, for example an alkali metal of base (i.e., sodium hydroxide) per mole of 105 hydroxide. The desired α -oxy or α -thio- β a-hydroxy-\(\beta\)-sulfosuccinic acid yields the sulfosuccinate may then be recovered and monosodium salt; the use of two moles of purified using conventional techniques. sodium hydroxide, the disodium salt and the The α - substituted - β - sulfosuccinate use of three moles of sodium hydroxide, the salts wherein the a-substituent is joined to trisodium salt. When R is carboxymethyl, the a-carbon atom of the sulfosuccinate moiety carboxyethyl, sulfomethyl or sulfoethyl, a by an SO SO₂ linkage may be prepared by tetrasalt can also be obtained. Similarly, other treating the appropriate a-substituted thio-\(\beta\)bases, such as ammonium hydroxide and sulfosuccinate with hydrogen peroxide accordorganic amines, may be utilized in the same ing to the methods described on pages 471manner to afford the type of salt desired. 472 in the text, "Reagents for Organic Syn-115 According to the present invention, excellent thesis" Fieser and Fieser, published by John cleaning results can be obtained by using the Wiley & Sons, Inc., 1967. novel compounds described above as deterg-The α - substituted - β - sulfosuccinate ency builders with a wide range of detergent salts wherein the α -substituent is joined to the surface active materials and mixtures thereof a-carbon atom of the sulfosuccinate moiety by in any of the usual physical forms for such an amino function (as in Formula II) may compositions such as powders, beads, flakes, be prepared by reacting an appropriately substituted or unsubstituted primary or secondbars, tablets, noodles, liquids and the like. The builders can be used singularly, in com-

bination with each other as the sole builder in

the detergent composition or in combination

ary amine with alkali metal salts of sulfomaleic

acid. Typical amines suitable for reaction to

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with other well-known detergent builders such as sodium nitrilotriacetate, sodium ethylene-diaminetetraacetate, sodium tripolyphosphate, trisodium orthophosphate, sodium and potassium pyrophosphate, sodium polyacrylate, disodium oxydiacetate, trisodium citrate, trisodium carboxymethyloxysuccinate, salts of oxidized starches and sodium or potassium carbonate, as well as other conventional organic and inorganic builders.

When using the detergent compositions to wash clothes, the wash solutions should have a pH from about 7 to 12 and preferably from 9 to 11 throughout the washing cycle. Therefore, the presence of an alkaline buffer in the detergent composition is usually desirable particularly when the soil to be removed from the clothes has a high content of acidic components. Suitable buffers include any of the common organic and/or inorganic buffers such as monoethanolamine, diethanolamine, triethanolamine, sodium and potassium silicates, sodium and potassium carbonates and bicarbonates and the like.

In the detergent compositions, which are claimed in our copending divisional application No. 785/75 (Serial No. 1,398,422), the only essential ingredients are the detergent surface active material and the builder. The weight percent of the builder present in the detergent composition will range from 5 to 90% and preferably from 20 to 60% and more preferably 35-50% by weight of the total weight of the composition. When expressed as a weight ratio of builder to surfactant, the builders used in the instant invention will generally be present in a ratio of about 1:10 to about 10:1, and preferably 2:1 to 5:1 depending on the end use of whether a heavy-duty or light-duty detergent is desired. When the builders are used in mechanical dishwashing compositions, the ratio of builder to surfactant is from about 10:1 to about 50:1.

The detergent surface active compounds which can be used within the detergent compositions include anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof. A detailed description of such detergent compounds is to be found in the Specification of our Divisional Application referred to above.

Other materials which may be present in the detergent compositions in generally minor amounts are those conventionally present therein. Typical examples thereof include the well-known soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers such as sodium sulfate, optical brighteners, perborates, bleaches, bleach activators, enzymes, suds boosters, suds depress-

ants, germicides, fungicides, anti-tarnishing agents, cationic detergents, fabric softening agents and in the case of liquid compositions, opacifiers and organic solvents. The balance of the detergent compositions may be water or inert filler.

It has been discovered that when higher than normal levels of anionic, nonionic, ampholytic or zwitterionic surfactants are used with the sulfosuccinate derivative salts of this invention, the detergency of the formulation is significantly enhanced particularly at low formulation concentrations (~ 0.1%) which are typically used by the housewife. For enhanced results the detergent formulation should contain surfactant levels of about 25% to about 45% by weight and the sulfosuccinate derivative salt levels of about 25% to about 75% by weight in the cases where the surfactants are anionic, ampholytic or zwitterionic. When the surfactant is a nonionic, enhanced detergency results are obtained when the level of said nonionic in the formulation is from about 15% to 30% by weight and the level of sulfosuccinate derivative salt is from about 25% to about 85% by weight.

In addition to their use in general household detergent compositions, the builders of the present invention find utility as boiler scale removers, stain removers and general chelating agents. When used at pH's of about 2 to about 5 as partially neutralized alkali metal, ammonium or substituted ammonium salts, especially in combination with wetting agents and surfactants, the compounds of the invention are excellent metal cleaning compounds.

EXAMPLE 1.

Table 1 below illustrates detergent compositions containing the detergency builders of the present invention in combination with representative classes of surface active agents compared with control or standard phosphatebuilt detergent compositions. The compositions were prepared by blending together the recited components in the proportions indicated, including an anticorrosive agent and buffer agent (sodium silicate), and the balance being water. The compositions were then tested on vacuum cleaner dust soiled cloth for detergency or cleaning ability in the Terg-O-Tometer test; wherein washing conditions are as indicated and the results reported as detergency units. The average detergency units (DU) of the formulation is the final reflectance of the soiled cloth, the reflectances 115 being obtained by measurement with a Gardner automatic color difference meter, Model AC-3.

50 50 50 50 50 50 y-ethoxy)a stroxya stroxya	Component						°C	% Composition	-	TABLE	н					Ċ	<u>.</u>	3	•	:		
xy)a 50 50 xya xya 10 10 10 10 10 10 10 10 10 10 10 10 10 1	a-hydroxya	50	20	50		1	1									5	litti Ois	8	Sodino	TELOM		
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849a 10 10 10 10 10 10 10 10 10 10 10 10 10 1	a-methoxya					٠				20												
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10 10 10 10 10 10 10 10 10 10 10 10 10 1	Nas P ₃ O ₁₀																			50	20	Ç
18 18 20 18 18 18 20 18 18 20 20 20 20 20 20 20 20 20 20 20 20 20	Sodium silicate (SiO ₂ :Na ₂ O=2.4:1)	10	10	10	01	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	01	2 2
18 18 20 20 18 18 18 18 18 18 18 18 18 18 18 18 18	Anionicb	18					8	36	18	18	18	18	18	18	18							
20 18 18 18	Anionicc		18													18				~		
18 18 4 balance 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	Vonionicd			20													20				20	
18 balance 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	Ampholytice				18													28			2	2
balance 0.2 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	Zwitterionic f					18												-	Š			2
0.2 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	Vater	1				-						balan	93						2			
24.6 24.4 26.5 23.1 25.6 26.1 24.7 27.1 23.0 24.2 15.4 22.3 4.8 6.4 16.1 19.9 18.8 20.1 28.7	ormulation Concentration, %	0.2	0.2	0.2			0.2	0.1	0.2	0.2	0.2	.0.2					0.2	0.2	0.2	0.2	0.2	0.2
	Detergency (DU's)	24.6	24.4	26.5	23.1	25.6	26.1	24.7	27.1	23.0	24.2	15.4	22.3			16.1	19.9	18.8	20.1	28.7	29.4	28.5

_		98,421	6
5	Sodium salts of α-substituted-β-sulfosuccinate Sodium linear secondary alkyl (C ₁₀ —C _{1s}) benzene sulfonate Sodium C _{1s} —C _{1s} α-olefin sulfonate C ₁₁ —C _{1s} linear secondary alcohols ethoxylated with 7 moles ethylene oxide/mole alcohol	7.04 gm of sodium hydroxide in 50 ml water is then added and the mixture heated at 60° C for 2 hours. The heated mixture is then extracted three times with 300 cc portions of	65
10	"Sulfobetaine DCH (cocodimethylsulfopropylbetaine) Washing conditions—180 ppm (2:1 Ca ⁺⁺ /Mg ⁺⁺); 120° F: pH 10 The following Examples 2 to 11 show	fraction is then filtered, washed with additional acetone and dried to give 16.2 gm of the title compound (structure confirmed by NMR and ion exchange of a sample followed by titration with standard sodium hydroxide: neutralization equivalent: found 147.0, theory 149.3).	70
15	succinates. α -substituted- β -sulpho-	EXAMPLE 5. Preparation of Trisodium ca-Dodecylorya	75
20	EXAMPLE 2. Preparation of Trisodium α-thio substituted- β-Sulfosuccinate Sulfomaleic anhydride was prepared by heating a mixture of 1 mole of sulfur trioxide with 1 mole of maleic anhydride first at 60° C	oxyethanol in place of the n-dodecanol there is obtained trisodium α-dodecyloxyethoxy-β-sulfosuccinate.	80
25	until the exothermic reaction subsided and then at 100—110° C for 3 hours. Forty-five gm of sulfomaleic anhydride product was then mixed with 45 gm of ice and the resulting solution extracted 25 times with 50 ml portions of ether to remove maleic acid. A 20 ml	EXAMPLES 6—8. Using n-tetradecanol in place of n-dodecanol in the procedure of Example 4 and carrying out the hydrolysis step with 10% excess aqueous sodium hydroxide at 80°C for 4 hours instead of 60°C at 2 hours, there is obtained exications.	85
30	collected, adjusted to pH = 8.6 with sodium hydroxide and refluxed for 4 hours. Then, an aqueous solution containing excess sodium methyl or ethyl mercaptide is added and the	succinate (Example 6). Similarly, using n- hexadecanol in place of n-dodecanol, there is obtained trisodium α-hexadeculoxy θ curls	90
35	The reaction mixture is then passed through a column of cation exchange resin and the effluent to low volume. The part is then	succinate (Example 7); using n-octadecanol, there is obtained trisodium α -octadecyloxy- β -sulfosuccinate (Example 8). EXAMPLE 9.	95
40	adjusted to 8.5 with sodium hydroxide and the solution evaporated to dryness. In this way, there is afforded trisodium α -methylthio- β -sulfosuccinate or trisodium α -ethylthio- β -sulfosuccinate.	Preparation of Trisodium c ₁ -Hydroxyethoxy- β-Sulfosuccinate Sulfomaleic anhydride (20 gm) is mixed with 37.2 gm (0.6 mole) of ethylene glycol and heated at 80° C for 4 hours. A solution of	100
45	EXAMPLE 3. Preparation of Trisodium α-Ethoxy-β- Sulfosuccinate Sulfomaleic anhydride, 3.9 gm, was dissolved in 25 ml of ethanol and refluxed for 5 hours. Then, 24 gm of 25% sodium ethoxide in ethanol was added and the	75 ml of water is then added and the mixture heated at 80° C for 4 hours. The mixture is then mixed with acetone to precipitate trisodium $-\alpha$ - hydroxyethoxy - β - sulfosuccinate, which is purified by repeated extractions with hot acetone to remove all ethylene gives	105
50	was then evaporated and the residue was dissolved in 100 ml of water and beated for	and water followed by filtration and drying in an oven. EXAMPLE 10.	110
55	1 hour at 80° C. The solution was then de- colorized with 5 gm of charcoal, filtered and evaporated. The crude residue of trisodium α -ethoxy- β -sulfosuccinate was purified by trituration with acetic acid and then filtered, washed with acetone and dried.	Preparation of the Tetrasodium Salt of cr-Carboxymethyloxy-β-Sulfosuccinic Acid Sulfomaleic anhydride (19.4 gm) is heated to 60° C and combined with 76 gm of ethyl glycolate. After heating the mixture at 80° C for 5 1/2 hours, there is added a solution of	115
60	EXAMPLE 4. Preparation of Trisodium α-Dodecyloxy-β- Sulfosuccinate Sulfomaleic anhydride (10 gm) are mixed with 80 gm (0.45 mole) of n-dodecanol and	45 gm of sodium hydroxide dissolved in 135 gm of water and heating is continued at 80° for an additional three hours. The mixture is then diluted with water and passed through a column of a cation exchange resin. The resulting eluent is then evaporated in vacuo to	120

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a low volume and the concentrate extracted repeatedly with acetone to remove glycolic acid and other impurities. The resulting extracted residue is then dissolved in water and the pH of the solution adjusted to 8.6 with dilute sodium hydroxide. Evaporation of the solution in vacuo and drying over P_2O_5 gives a residue of the tetrasodium salt of α -carboxymethyloxy- β -sulfosuccinic acid.

EXAMPLE 11.

Prepartion of Trisodium α₋(2-Hydroxy-ethylamino)-β-Sulfosuccinate
Sulfomaleic anhydride (prepared from a 1/1 ratio of SO₃/maleic anhydride by heating the mixture at 100—110° C for 3 hours; active content, 86%) 20.7 gm (0.1 mole), was added to 100 gm of ice. The resulting solution was kept at 10—15° C and neutralized to

pH = 8.6 by slowly adding 28.4 gm of 50% sodium hydroxide. Monoethanolamine, 6.1 gm (0.1 mole), was next added slowly and the temperature allowed to rise to room temper-

ature. After standing overnight, the reaction mixture was poured into 800 ml of acetone. The solvent was then decanted from the resulting syrupy lower layer and the latter reprecipated three times from water with fresh acetone. The residue was then dried in a dessicator over P_2O_5 to give 38.8 gm of an off-white, granular product containing approximately 88% trisodium - α - (2 - hydroxyethylamino) - β - sulfosuccinate by tritration with perchloric acid. The structure was confirmed by NMR analysis.

The above method is satisfactory for reacting water-soluble amino compounds with sulfomaleic anhydride. For water insoluble amino compounds such as the higher alkyl amines, a mixed solvent system such as ethanol/water and dioxane/water is used together with temperatures in the range of 25—80° C.

Table 2 indicates the reactants required to obtain other α - substituted - β - sulfosuccinate salts having the R and Z moieties set forth in Formula I, following the procedures of the appropriate examples.

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,	T	TABLE 2	
~	2	Example	Example Reactants (Sulfomaleic Anhydride +)
Ethyl	0	6	ethanol
Alkyl (C ₁ -C; ₀)	0	4 8-8	CC., primary, secondary or tertions slocked
Phenyi	0	48	Phenol
Carboxyphenyl	0	0	Methy saliculate
(C,-C, Alkylphenyl	0	8-1	(C ₁ -C ₄) Alkylphenoi
o, m, p methylphenyl or methylisopropyl phenyls	0	4-8	o, m, p cresol, carvacrol, thymol
H 00C-CH ₂ -	0	01	Ethyl glycolate
H00C-CH2CH2-	0	01	Methyl-B-hydroxypropionate
HO,S-CH2CH2-	0	4	Isethionic acid
R'O(CH,CH,O)n-CH,CH,-	0	4	R'O(CH.CH.O)CH.CH OH
HOCH,CH,OCH,CH,-	0	4	HOCH, CH, OCH, CH, OH
H0(('H,CH,0),CH,CH,-	0	4	но(си,си,си,си,он
HO(C'H,CH,O) ₁₀ CH,CH,-	0	4	но (СН, СН, СН, СН, СН, СН, СН, СН, СН, СН,
HO(CH,CH,O),5CH,CH,-	0	4	но(сн,сн,о), сн,сн,он
CH,CH,O(CH,CH,O),CH,CH,-	0	4	CH,CH,CH,CH,CH,CH,CH,OH
CH,(CH,),0(CH,CH,0),CH,CH,-	0	4	CH,(CH,),,0(CH,CH,O),CH,CH OH
CH ₃ (CH ₂) _{3,0} 0(CH ₂ CH ₂ O) ₃ CH ₃ CH ₂ -	0	. 4	CH,(CH,),,0(CH,CH,0),CH,CH
CH,CH,S(CH,CH,O),CH,CH,-	0	4	CH,CH,S(CH,CH,O),CH,CH,OH
CH,CH,S(CH,CH,O),CH,CH,-	0	4	CH,CH,S(CH,CH,O),CH,CH,OH

	TAB	TABLE 2 (Continued)	tinued)
œ	Z	Example	Example Reactants (Sulfomaleic Anhydride +)
HOCH2CH2-	0	6	Ethylene glycol
HOCH, CH, CH, -	0	6	Trimethylene glycol
HOCH2(CH2),CH2-	0	6	Hexamethylene glycol
Methyl or ethyl	S	6	Sodium methyl or ethyl mercaptide
Alkyl (C ₃ -C ₃₀)	S	4-8	C ₃ -C ₃ 0 alkylmercaptan
Phenyl	S	4-8	Thiophenol
Carboxyphenyl	S	10	Methyl 2-mercaptobenzoate
Alkyiphenyl	S	4-8	Alkylthiophenol
H00C-CH ₂ -	S	10	Ethyl mercaptoacetate
H00C-CH ₂ -CH ₂ -	SO	10	Methyl <i>B</i> -mercaptopropionate
HO ₃ SCH ₂ CH ₂ -	S	4	Mercaptoethanesulfonic acid
R'O(CH,CH,O)nCH,CH,-*	S	4	R'O(CH2CH2O)nCH1CH2SH*
HOCH,CH,OCH,CH,-	S	2	HOCH, CH, OCH, CH, SNa
HO(CH2CH2O)3CH2CH2-	S	2	HO(CH2CHO), CH2CH2SNa
HO(CH,CH,0),CH,CH,-	S	7	HO(CH,CH,O),OCH,CH,SNa
HO(CH ₂ CH ₂ O) ₁₅ CH ₂ CH ₂ -	S	2	HO(CH,CH,O)15 CH,CH,SNa
CH,CH,O(CH,CH,O),CH,CH,-	S	4	CH,CH,O(CH,CH,O),CH,CH,SH
CH,(CH,),,0(CH,CH,0),CH,CH,-	S	4	CH ₃ (CH ₂) ₁₁ (CH ₂ CH ₂ O) ₉ CH ₂ CH ₂ SH
CH,(CH,),,0(CH,CH,0),CH,CH,-	S	4	CH ₃ (CH ₂) _{1,} O(CH ₂ CH ₂ O) ₃ CH ₂ CH ₂ SH

£	TABLE 2 (Continued)	2 (Cont	inued)
~	2	Exampl	Example Reactants (Sulfomaleic Anhydride +)
CH,CH,S(CH,CH,CH,-	S	4	CH,CH,CH,CH,SH
CH,CH,CH,CH,O),CH,CH,-	S	4	CH, CH, SICH, CH, O), CH, SH
HOCH, CH, -	S	7	Sodium 2-hydroxvethylmercanida
HOCH,CH,CH,-	S	7	Sodium 3-hydroxynrony [mercentide
HOCH,(CH,),CH,-	S		Sodium 6-hydroxyhexylmercantide
Methyl or ethyl	SO	2	Methyl or ethyl mercaptana
Alkyl (C,-C,0)	80	48	C,-C, alkylmercaptana
Phenyl	SO	48	Thiophenol ^a
Carboxyphenyl	SO	10	Methyl 2-mercaptobenzoatea
C,-C, alkylphenyl	SO	4-8	Alkylthiophenola
H00C-CH2-	80	10	Ethylmercaptoacetatea
H00C-CH,CH,-	SO	10	Methyl β-mercaptopropionatea
R' O(CH, CH, O), CH,*	80	s	R'O(CH,CH,O),CH,CH,SHa *
HOCH,CH,-	80	7	Sodium 2-hydroxyethylmercaptide
носн,сн,сн,-	SO	7	Sodium 3-hydroxypropy/mercaptide
но(сӊсн²),сн²	SO	7	Sodium 6-hydroxyhexylmercaptide
a Followed by oxidation to sulfoxide according to Fieser reference.	er referen	ce.	
	so,	7	C,-C, alkylmercaptanb
C,-C,0 alkyl	SO ₂	88	C ₃ -C ₁₀ alkylmercaptan ^b

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Z Example Reactants (Sulfomaleic Anhydride +)	SO ₂ 4-8 Thiophenolb	SO ₂ 4-8 Methyl 2-mercaptobenzoateb	SO ₂ 10 Ethyl mercaptoacetateb	SO ₂ 10 Methyl 2-mercaptobutyrateb	
Ж	Phenyl	Carboxyphenyl	H00C-CH ₂ -	HOOC-CH2CH2CH2-	R' 0(CH,CH,0),CH,CH,_*

b Followed by oxidation to sultone according 'o Fieser reference.

* wherein R₁ is hydrogen or a C₁-C₂₄ alkyl group.

wherein R' is hydrogen or alkyl containing 1—24 carbon atoms and n is 0 or an integer of 1—15; and Z is O, S, SO₂, SO, WHAT WE CLAIM IS:—
1. An α - substituted - β - sulfosuccinic acid having the general formula:

 Θ $R-Z-CH-CH-SO_3H$ соон соон

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or an alkali metal, ammonium or substituted ammonium salt thereof; wherein R is (C₁—C₂, alkyl, (C₁—C₂, hydroxyalkyl or (C₂—C₃, alkoxyalkyl; phenyl; carboxysubstituted or mono-, di- or tri-alkyl-substituted phenyl wherein each of the alkyl groups contains 1—4 carbon atoms; sulfoalish or carboxyalkyl wherein the alkyl moieties contain 1—4 carbon atoms; or

10

R'Z(CH2CH2O),—CH2CH2—

15

or NR, wherein R, is hydrogen or R as defined above; when Z is o←¤

20

25 or NR₁ the groups R may be joined with the nitrogen atom to form a morpholinyl group, and when Z is O and the group R is an alkyl group the latter contains 2—30 carbon atoms.

			12
5	2. A compound as claimed in claim 1 wherein Z is oxygen. 3. A compound as claimed in claim 1 or claim 2 wherein R is an alkyl group containing 2—24 carbon atoms. 4. A compound as claimed in altitudes.	wherein R is an alkyl group containing 1—8 carbon atoms. 17. α - dodecylthio - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof.	40
10	4. A compound as claimed in claim 3 wherein R is an alkyl group containing 9—24 carbon atoms. 5. A compound as claimed in claim 3	18. α - hexadecylthio - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 19. α - octadecylthio - β - sulfosuccinic	45
10	wherein R is an alkyl group containing 2—8 carbon atoms. 6. α - dodecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted	acid or an alkali metal, ammonium or substituted ammonium salt thereof. 20. A compound as claimed in claim 1 wherein Z is SO.	50
15	7. α - hexadecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof.	21. A compound as claimed in claim 1 wherein Z is SO ₂ . 22. A compound as claimed in claim 1 having the general formula:	55
20	 8. α - octadecyloxy - β - sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 9. An α-hydroxyalkoxy (2—24 carbon atoms)-β-sulfosuccinic acid or an alkali metal, ammonium or substituted ammonium salt 	$R - N - CH - CH - SO_sH$ $R_1 COOH COOH$ (II)	
25	10. A hydroxyethoxy compound as claimed in claim 9. 11. An α-alkoxy (1—24 carbon atoms)-ethoxy-β-sulfosuccinate as claimed in claim 1.	wherein the groups R and R ₁ may be the same or different, and R is C ₁ —C ₂₀ alkyl; C ₁ —C ₄ hydroxyalkyl; carboxymethyl; carboxyethyl; sulfomethyl; sulfoethyl; or R and R ₁ may be joined with the nitrogen atom to form a	60
30	succinic acid or an alkali metal, ammonium or substituted ammonium salt thereof. 13. A compound as claimed in claim 1 wherein R is a carboxymethyl group.	morpholinyl moiety; and R ₁ is hydrogen or R. 23. A compound as claimed in claim 1 substantially as described herein with reference to any of Examples 2—11 and in Table 2.	65
35	14. A compound as claimed in claim 1 wherein Z is sulfur. 15. A compound as claimed in claim 14 wherein R is an alkyl group containing 1—24 carbon atoms. 16. A compound as claimed in claim 14	R. V. TATE, Chartered Patent Agent Unilever Limited, Blackfriars, London, E.C.4.	

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